

Linking density functional and mode coupling models for supercooled liquids

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Abstract

We compare predictions from two familiar models of the metastable supercooled liquid respectively constructed with thermodynamic and dynamic approach. In the so called density functional theory (DFT) the free energy $F[\rho]$ of the liquid is a functional of the inhomogeneous density $\rho(\mathbf{r})$. The metastable state is identified as a local minimum of $F[\rho]$. The sharp density profile characterizing $\rho(\mathbf{r})$ is identified as a single particle oscillator, whose frequency is obtained from the parameters of the optimum density function. On the other hand, a dynamic approach to supercooled liquids is taken in the mode coupling theory (MCT) which predict a sharp ergodicity-nonergodicity transition at a critical density. The single particle dynamics in the non-ergodic state, treated approximately, represents a propagating mode whose characteristic frequency is computed from the corresponding memory function of the MCT. The mass localization parameters in the above two models (treated in their simplest forms) are obtained respectively in terms of the corresponding natural frequencies depicted and are shown to have comparable magnitudes.

I. INTRODUCTION

The dynamics of a liquid supercooled below its freezing point slows down drastically. The relaxation time of the liquid increases sharply with supercooling so that below a temperature, generally termed as a calorimetric glass transition temperature T_g , the liquid stops flowing and behaves like a solid with elastic properties. The amorphous solid is in a metastable equilibrium state with its constituent particles vibrating around their respective parent sites which form a disordered lattice without any long range order. Over time scales of structural relaxation such a description persists. The issue of an underlying thermodynamic transition in the supercooled liquid accompanying this vitrification process into a solid has been studied in different models [1]. For describing the amorphous solid like state both thermodynamics and dynamics based models have been proposed.

We first outline the thermodynamic approach. The transition of the dense liquid into a crystalline state with long range order occurs at the freezing point. This transition is of thermodynamic origin. An order parameter based model for understanding the freezing transition and the inhomogeneous crystalline state is provided in the density functional theory (DFT) [2–4]. The density functional approach to describe the freezing phenomena [5, 6], has a statistical mechanical basis. This method has also been extended to describe the supercooled liquid state. Metastable minima of the free energy functional intermediate between the crystal and the liquid, have been observed by several authors [7–10] in the past. The amorphous state is characterized with an inhomogeneous density $\rho(\mathbf{r})$ having peaks centered around a set of points $\{\mathbf{R}_i\}$, constituting an amorphous lattice without any long range order. In DFT, sharply localized peaks of the density profiles are identified as representing individual particles vibrating around a lattice site. The width of the density profile signifies the average displacement of the particle around the lattice site. This width is required to remain within a limit [11] in order for the solid like state to survive. Using the average particle displacement from the DFT to the average potential energy, the spring constant and hence the natural frequency for the oscillator presenting the single particle dynamics is obtained.

Next we consider the model based on dynamics of the liquid. The mode coupling theory (MCT) is a formulation extensively developed over last thirty years for understanding slow relaxation in a strongly correlated liquid. Using a microscopic approach, MCT has provided

a model for understanding the slow dynamics at the initial stage of supercooling of the metastable liquid [12–14]. The dynamics of the fluid is described in terms of that of the slow modes which reflects the conservation laws in the fluid. In the deeply supercooled state, solid like behavior with finite shear modulus develops [15] and manifests through existence of transverse sound modes characteristic of the solids. From a theoretical level this is understood in terms of Goldstone modes which appear in the glassy states [16, 17] and has been used to explain characteristic features [18, 19] of the amorphous states. The MCT in its simplest form predicts a transition from the ergodic liquid state to a non-ergodic glassy state. The latter is characterized by a finite shear modulus. The MCT is based on the equations of microscopic dynamics[20] of a set of fluid particles. The equations of fluctuating nonlinear hydrodynamics (FNH) which give rise to the basic equations of the MCT, involve a driving free energy functional $F[\psi]$, expressed in terms of the slow modes $\{\psi\}$ of the fluid. The free energy functional for the liquid is dependent on the density function $\rho(\mathbf{r})$. Thus equations of FNH are obtained using the same free energy functional as that of standard DFT. The stationary state for the fluid is described by the solution $\exp[-F(\psi)]$. The form of the memory function [21] giving rise to the oscillatory behavior of the single particle correlation is obtained from these equations [22].

Kirkpatrick and Wolynes first demonstrated [23] the link between the two basic models of the metastable liquids and obtained the mass localization parameter in amorphous state. In the simplified model these authors used the so called vineyard approximation to link the collective and single particle density correlations. It was shown that the spring constant for the vibrating particle is obtained using respectively the description based on static and dynamic considerations. From a static or thermodynamic point of view the spring constant can be inferred from the equilibrium density distribution in the inhomogeneous state. On the other hand in a dynamical approach, the spring constant is obtained from the frequency of the propagating oscillatory mode in the non-ergodic state. The spring constant for vibrating particle is computed from the long time limit of the corresponding memory function of the MCT. In the present work we explore this link on the DFT and MCT descriptions of the amorphous state. We compare the two models by explicit computation of the corresponding localization parameters with a DFT and MCT approach. The structure function of the uniform liquid state and assumption of an amorphous lattice are the only required inputs in the comparison between the two models. The paper is organized as follows. In the next

section we discuss briefly the formulation of the density functional model and show how the optimum value of the mass localization parameter follows from purely thermodynamic considerations. Next, in section III we discuss the dynamic model demonstrating how the mode coupling approach is used to obtain the natural frequency of the single particle mode in the metastable liquid. In section IV, we discuss how the MCT and the DFT are linked. In section V we present numerical results focusing on the key quantity for comparing the two models. We end the paper with a brief discussion of the results.

II. THE THERMODYNAMIC MODEL

In the thermodynamic approach, a generalized free energy functional reaches a local minimum corresponding to the metastable glassy state. The free energy functional is treated as a function of the density which depicts the inhomogeneous mass distribution in the supercooled liquid. We present below briefly the calculation of the free energy.

A. Density functional theory

Using the thermodynamic extremum principle for the free energy functional $F[\rho(\mathbf{r})]$, the inhomogeneous density $\rho(\mathbf{r})$ for the equilibrium state is obtained. The total free energy is a sum of two parts, the ideal gas term and the interaction or the so called excess contribution, respectively denoted as F_{id} and F_{ex} :

$$F[\rho(\mathbf{r})] = F_{\text{id}}[\rho(\mathbf{r})] + F_{\text{ex}}[\rho(\mathbf{r})]. \quad (1)$$

The ideal gas part of the free energy functional is generalized for non-uniform density $\rho(\mathbf{r})$ as

$$F_{\text{id}}[\rho(\mathbf{r})] = k_B T \int d\mathbf{r} \rho(\mathbf{r}) (\ln[\Lambda^3 \rho(\mathbf{r})] - 1). \quad (2)$$

The excess part is also obtained as an expansion in terms of the density fluctuations. The density function $\rho(\mathbf{r})$ signifies the nature of the mass distribution in the inhomogeneous state. The free energy $F[\rho]$ of the solid state is obtained in terms of the density fluctuations, by using a functional Taylor expansion around the uniform liquid state. We consider perturbation expansion of the excess free energy around a uniform system of density same

as the average density of the corresponding inhomogeneous structure.

$$\rho_0 = \frac{1}{V} \int d\mathbf{r} \rho(\mathbf{r}) \quad . \quad (3)$$

The functional Taylor series expansion about the homogeneous density distribution ρ_0 is given as [5],

$$\begin{aligned} \beta F[\rho(\mathbf{r})] - \beta F(\rho_0) = & \int d\mathbf{r} \rho(\mathbf{r}) \ln \left(\frac{\rho(\mathbf{r})}{\rho_0} \right) \\ & - \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2) c(\mathbf{r}_1 - \mathbf{r}_2; \rho_0) \quad , \end{aligned} \quad (4)$$

where $c(r; \rho_0)$ is the Ornstein-Zernike two point direct correlation function [24] for the uniform liquid of density ρ_0 . Here $\delta\rho(\mathbf{r})$ is the deviation of the inhomogeneous state density $\rho(\mathbf{r})$ from the average density ρ_0 . The free energy functional $F[\rho]$ is minimized with respect to an optimum choice for the inhomogeneous density function $\rho(\mathbf{r})$. The density function is chosen a parametric form signifying localized density profiles centered on a set of lattice points for which we need a specific underlying lattice $\{\mathbf{R}_i\}$ as an input.

B. The Oscillator model

In this the metastable glassy state is characterized as one in which the individual particles are oscillating around a set of lattice sites $\{\mathbf{R}_i\}$ situated on a random lattice. The degree of mass localization in the metastable state of the supercooled liquid is identified from $\rho(\mathbf{r})$ for which the free energy $F[\rho]$ reaches a local minimum. The test density function which has been most effectively used [25] in the DFT is in terms of normalized gaussian functions centered around a set of lattice points $\{\mathbf{R}_i\}$.

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi} \right)^{3/2} \sum_{\mathbf{R}_i} e^{-\alpha(\mathbf{r}-\mathbf{R}_i)^2} \equiv \sum_{i=1}^N \phi_\alpha(|\mathbf{r} - \mathbf{R}_i|) \quad (5)$$

where $\phi_\alpha(r) = (\alpha/\pi)^{3/2} \exp(-\alpha r^2)$. The density is parameterized in terms of the mass localization parameter α which is inversely proportional to the square of the width of Gaussian profiles in the expression on the right hand side of Eqn. (5). The parameter α quantifies the motion of particles in the system in a coarse grained manner. The $\alpha \rightarrow 0$ limit depicts gaussian profiles of infinite width and thus the corresponding phase represents the homogeneous liquid state. Increasing values of α represent increasingly localized structures and thus

referring to greater inhomogeneity in the system. The α corresponding to the free energy minima determines the preferred thermodynamic phase. For simplicity we assume that the α values at the different sites are the same though in reality they are different characteristic of the heterogeneous state [26, 27].

In case of completely non overlapping Gaussian profiles, the situation corresponds to individual particles oscillating around their mean positions which form an underlying lattice. In case of a crystal this lattice has long range order while for an amorphous solid this is a random structure representing a metastable liquid. In the harmonic solid the spring constant κ_s , for the oscillation of a single particle around the lattice site, is simply related to the width parameter α for the gaussian profiles. The average kinetic and potential energies of an oscillator with position and momentum coordinates $\{x, p\}$ are same and each is equal by the law of equipartition to $(k_B T)/2$, *i.e.*,

$$\frac{\langle p^2 \rangle}{2m} = \frac{\kappa_s}{2} \langle x^2 \rangle = \frac{k_B T}{2} . \quad (6)$$

On the other hand, corresponding to the DFT expression for the density (5) the average mean square displacement for the single particle is given by, $\langle x^2 \rangle = 1/(2\alpha)$. Using this in the above relation we obtain

$$\alpha = \frac{\kappa_s}{2k_B T} \quad (7)$$

Therefore the characteristic frequency ω_0 of the oscillator is obtained as

$$\omega_0^2 = \frac{\kappa_s}{m} = 2v_0^2 \alpha , \quad (8)$$

where $v_0^2 = k_B T/m$ is the thermal speed.

For the metastable harmonic solid held at a finite temperature the width parameter for the inhomogeneous density function is obtained by invoking the standard thermodynamic extremum principles. The free energy of the metastable liquid is obtained by evaluating the corresponding density functional expression with a test density function for inhomogeneous state. The latter is parameterized in terms of the width parameter α . The optimum value of $\alpha \equiv \alpha_{\text{DFT}}$ (say) corresponding to which the free energy is a minimum presents the metastable state. Since the particle positions are strictly localized in this case, the width parameter $\alpha \sigma^2 \gg 1$, where σ is a microscopic length scale associated with the interaction potential of the liquid particles.

III. THE DYNAMIC APPROACH

The self-consistent mode coupling theory (MCT) presents a microscopic model for understanding the slow relaxation behavior seen in a supercooled liquid using a dynamic approach. The dynamics of the dense liquid is generally described in terms of that of a set of slow modes which signify the conservation laws for the fluid. The equations of motions for these modes are the balance equations representing the underlying conservation laws. The MCT is formulated by taking in to account the effects of the nonlinearities present in these equations on the transport properties of the liquid. We briefly outline below how the equations of generalized hydrodynamics give rise to the MCT equations for glassy dynamics.

A. Generalized Hydrodynamics

The generalized Langevin equation, leads to the equations of motion for the respective coarse grained densities of mass and momentum as $\psi_i \equiv \{\rho(\mathbf{r}, t), \mathbf{g}(\mathbf{r}, t)\}$ for a one component liquid. Following standard procedures[28] we obtain:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{g} = 0, \quad (9)$$

$$\frac{\partial g_i}{\partial t} + \nabla \cdot (g_i \mathbf{v}) + \rho \nabla_i \frac{\delta F_U}{\delta \rho} - L_{ij}^0 v_j = \theta_i \quad . \quad (10)$$

In the following we use the convention that repeated indices are summed over. The field $\mathbf{v}(\mathbf{r}, t)$ is defined in terms of the nonlinear constraint $\mathbf{g} = \rho \mathbf{v}$ and represents $1/\rho$ nonlinearity in the equations fluctuating nonlinear hydrodynamics. L_{ij}^0 represents the matrix of bare or short time viscosities. These dissipative coefficients are related to the correlation of the gaussian noises respectively in Eqns. (10).

$$\langle \theta_i(\mathbf{r}, t) \theta_j(\mathbf{r}', t') \rangle = 2\beta^{-1} L_{ij}^0 \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad . \quad (11)$$

Here β^{-1} denotes the Boltzmann factor determining the strength of the thermal noise correlations. For an isotropic system the bare viscosity matrix L_{ij}^0 involves two independent coefficients.

$$L_{ij}^0 = \Gamma_0 \nabla_i \nabla_j + \varsigma_0 (\delta_{ij} \nabla^2 - \nabla_i \nabla_j) \quad (12)$$

where Γ_0 and ς_0 respectively denotes the bare or short time longitudinal and shear viscosities. The stationary solution of the Fokker-Planck equation corresponding to the above stochastic

equations is e^{-F} with $F[\psi]$ being identified as the free energy functional of the local densities $\{\psi(\mathbf{r}, t)\}$. F is expressed as

$$F[\rho, \mathbf{g}] = F_K[\rho, \mathbf{g}] + F_U[\rho], \quad (13)$$

where the kinetic part dependent on momentum density \mathbf{g} is obtained as [29]

$$F_K = \int d\mathbf{r} \frac{g^2(\mathbf{r})}{2\rho(\mathbf{r})} . \quad (14)$$

The $1/\rho$ nonlinearity in the expression for F_K is important in producing the form of the equations of fluctuating nonlinear hydrodynamics (FNH) for the set $\{\rho, \mathbf{g}\}$. The so called potential part $F_U[\rho]$ which is a functional of density only and is identified with the expression (4) of the free energy functional $F[\rho]$ in terms of the inhomogeneous density function $\rho(\mathbf{r})$ used in the DFT. Using the leading order correction to the transport coefficients in the renormalized correlation function, the simplest form of the mode coupling model follows. This model predict a sharp ergodicity-nonergodicity (ENE) transition at a critical density arising from a nonlinear feedback mechanism due to coupling of dominant density fluctuations. The transition is defined in terms of the long time limit of the normalized collective density correlation function $\phi(q, t)$.

$$\phi(q, t \rightarrow \infty) = f(q) . \quad (15)$$

$f(q)$ is referred to as the corresponding non-ergodicity parameter at wave number q for the collective density correlation function. As the transition is approached from the liquid side, $f(q)$ is nonzero beyond the ENE transition. In the non-ergodic state $f(q)$ remains nonzero and shows interesting scaling behavior [30, 31] in the vicinity of the ENE transition point. The mechanism for slow dynamics is understood in terms of the Laplace transform of the correlation functions. The Laplace transform of $\phi(q, t)$ is given by

$$\phi(q, z) = \left[z - \frac{q^2 c_0^2}{z + iq^2 L(q, z)} \right]^{-1} \quad (16)$$

where c_0 is the speed of sound and $L(q, z)$ is the generalized transport coefficient or the memory function. The generalized longitudinal viscosity $L(q, z)$ contains the bare and the mode coupling part, expressed as

$$L(q, z) = L_B(q) + L^{mc}(q, z) \quad (17)$$

The uncorrelated collisions occurring during the short time are responsible for the bare contribution $L_B(q)$ to the viscosity. The inverse Laplace transform of the mode-coupling contribution $L^{mc}(q, z)$ in equation (16) is given by

$$L^{mc}(q, t) = \frac{\beta^{-1}}{2\rho_0} \int \frac{d\mathbf{k}}{(2\pi)^3} V(\mathbf{q}, \mathbf{k}, \mathbf{k}_1) \phi(k, t) \phi(k_1, t) \quad (18)$$

where the vertex function V is,

$$V(\mathbf{q}, \mathbf{k}, \mathbf{k}_1) = S(k)S(k_1) [(\hat{\mathbf{q}} \cdot \mathbf{k}) c(k) + (\hat{\mathbf{q}} \cdot \mathbf{k}_1) c(k_1)]^2, \quad (19)$$

using the notation $\mathbf{k}_1 = \mathbf{q} - \mathbf{k}$. $c(k)$ is the fourier transform of Ornstein-Zernike direct correlation function $c(r)$ introduced in the expression (4) for the free energy. $S(k)$ is the static structure factor of the liquid. Taking F_U as a quadratic functional of the fields ρ , the eqn. of motion (10) for the momentum density \mathbf{g} gives rise to a cubic nonlinearity. The form of the vertex functions in the nonlinear terms of the momentum density (\mathbf{g}) equation is linked to the both the ideal gas and excess part of the free energy functional $F[\rho]$ in Eqn. (4) presented above.

B. Single particle dynamics

At the microscopic level the density of a tagged single particle in the fluid is a conserved property similar to the collective densities. The Laplace transform of the normalized correlation $\phi_s(q, t)$ is obtained in a form similar to that for $\phi(q, z)$:

$$\phi_s(q, z) = \frac{1}{z + iq^2 D_s(q, z)} \quad (20)$$

with the inverse of the renormalized self diffusion coefficient

$$D_s^{-1}(q, z) = \nu_0^{-1} + \Delta_{mc}(q, z) \quad (21)$$

The bare diffusion coefficient is $\nu_0 = \tau_0/(\beta m)$ where τ_0 presents a characteristic short time for the liquid dynamics [32, 33]. For the supercooled dense liquid the above memory function produces sharp fall in the tagged particle diffusion if we make the so called adiabatic approximation [22, 34]. The involves assuming that the density fluctuations decays much more slowly than the momentum fluctuations in the deeply supercooled state. With this approximation applied to the momentum density equation the current correlation functions

are simply expressed [22] in terms of density correlation functions. We obtain, at one-loop order, for the mode coupling part of the memory function for the inverse of $D_s(q, z)$

$$\Delta_{mc}(q, t) = \frac{1}{\rho_0} \int \frac{d\mathbf{k}}{(2\pi)^3} \left[(\hat{\mathbf{q}} \cdot \mathbf{k}) \frac{c(k)}{\tilde{\Gamma}_0(k)} \right]^2 \phi_s(k_1, t) \phi(k, t) S(k). \quad (22)$$

Δ_{mc} is dependent on the vertex function involving the wave vector dependent factor $\tilde{\Gamma}_0(k)$. The latter determines the variation of the sound attenuation or damping of density fluctuations over a range of length scales (k -values) starting from short distances. The correlation of the tagged-particle momentum also follows in a straightforward manner from the above analysis. The renormalized expression for the longitudinal tagged-particle current correlation is obtained as

$$F_s(q, z) = \frac{1}{z + \tau_0^{-1} + v_0^2 \Delta_{mc}(q, z)} \quad (23)$$

For the correlation of the single particle density, the corresponding long time limit of the correlation function is defined as

$$\phi_s(t \rightarrow \infty) = f_s(q) \quad . \quad (24)$$

$f_s(q)$ is referred to as the non-ergodicity parameter of self correlation function. Within the adiabatic approximation of fast relaxation of momentum fluctuations compared to that of density fluctuations, both $f(q)$ and $f_s(q)$ simultaneously become nonzero at the ENE transition. This is understood as follows: At the ENE transition the long time limit of $\phi(t)$ is nonzero *i.e.*, $\phi(z) \sim 1/z$ and the corresponding Laplace transform of the generalized transport coefficient $L^{mc}(z) \sim 1/z$ pole conforming to the physics of diverging the viscosity. Using the form (22) of the memory function obtained in the adiabatic approximation, it follows that Laplace transform of the corresponding memory function also has the same pole *i.e.*, $\Delta_{mc}(z) \sim 1/z$. Therefore the diffusion coefficient goes to zero at the ENE transition and beyond the ENE transition, $\phi_s(z) \sim 1/z$ implying that $f_s(q) \neq 0$. Taking the long time limit of Eq.(16) and (20) we get a set of self consistent integral equations for the respective non ergodicity parameters $\{f\}$:

$$\frac{f(q)}{1 - f(q)} = \mathcal{L}(q) \quad . \quad (25)$$

Here $\mathcal{L}(q)$ is the long time limits of the renormalized (longitudinal) viscosity $L^{mc}(q, t)/c_0^2$. The Percus-Yevick structure factor (with verlet-Weiss correction) is used as an input in solving the NEP equation (25) and (26). The inset of Fig.1 displays the solution of the

NEP equations for a hard sphere system at packing fraction $\eta = .525$. Using the values of the long time limits for the collective density correlations the corresponding single particle quantity f_s is obtained from the solution of the equation

$$\frac{f_s(q)}{1 - f_s(q)} = q^{-2}\gamma(q) \quad . \quad (26)$$

The functions $\gamma(q)$ is the long time limits of the renormalized memory function $\Delta_{mc}(q, t)$ scaled with the bare diffusion constant $\nu_0 = \gamma_0\chi_{cc}^{-1}$. Since the $\gamma(q)$ is finite in the $q \rightarrow 0$ limit, from Eqn. (26) it is clear that $f_s(q)$ remains pinned at the value 1. The $f_s(q)$ obtained using the $f(q)$ at density $\eta = .525$ is shown in Fig. 1.

IV. LINKING DFT WITH MCT

We now demonstrate that the results from the mode coupling models for the dynamics of the frozen supercooled liquid are linked to the static density functional description of the amorphous solid state. This link is established here focusing on the the tagged particle dynamics as predicted from the two different descriptions of the frozen solid. In the thermodynamic picture, the glassy state is characterized as one in which the individual particles are oscillating around a set of lattice sites $\{\mathbf{R}_i\}$ situated on a random lattice. On the other hand, in the simplest form of mode coupling theory which predict the sharp ENE transition, the self diffusion coefficient $D_s(q, z = 0)$ of the tagged particle becomes zero below the dynamic transition point. This also implies complete localization similar to the static problem. The key quantity for analyzing the single particle dynamics is the tagged particle density correlation function given by (20). The mode coupling effects are included here in terms of the self energy $\Delta_{mc}(0, t)$ given by eqn.(22). The form (22) of the mode coupling contribution to the memory function $\Delta_{mc}(0, t)$ is obtained in the adiabatic approximation. In MCT the transition of the supercooled liquid to the nonergodic glassy state occurs at a critical density. This transition is driven by a key feed back mechanism as a result of which the density correlation function freezes in the long time limit. Freezing of the density correlation function $\phi(q, t)$ thus implies that the Laplace transform of the memory function $\Delta_{mc}(z)$ develops a $1/z$ pole. In the small z limit we write for the memory function,

$$\Delta_{mc}(z) = \frac{\tilde{\gamma}_\infty}{z} + R.T \quad (27)$$

where $\tilde{\gamma}_\infty$ is the long time limit of $\Delta_{mc}(0, t)$,

$$\tilde{\gamma}_\infty = \Delta_{mc}(0, t \rightarrow \infty) \quad (28)$$

and R.T represents the regular terms. The development of the $1/z$ pole or non zero value for $\tilde{\gamma}_\infty$ is therefore crucial for the localized motion of the single particle signifying vibrating modes. Assuming the latter to be harmonic in nature a simple relation is reached between the corresponding spring constant and $\tilde{\gamma}_\infty$. The form (27) for the memory function, it follows from the denominator of the RHS of Eqn.(23) that the current correlations represent damped harmonic waves having pole structure $(z^2 - v_0^2 \gamma_\infty)^{-1}$. The latter represents vibration around the lattice sites. The corresponding frequency of oscillation ω_s and hence the spring constant κ_s of the vibration is obtained from the pole as

$$\omega_0^2 = v_0^2 \tilde{\gamma}_\infty \quad . \quad (29)$$

The above result for the frequency of the oscillator follows from a purely dynamical route (MCT) for the localized single particle dynamics. Now using the relation (8) the width parameter α obtained from the dynamical consideration, is related to the self energy $\tilde{\gamma}_\infty$ as,

$$\alpha_{\text{MCT}} = \frac{\tilde{\gamma}_\infty}{2} \quad . \quad (30)$$

The quantity $\tilde{\gamma}_\infty$ is obtained by taking the long time limit for the memory kernel $\Delta_{mc}(t)$. It follows from the result (22):

$$\Delta_{mc}(0, t) = \frac{1}{3\rho_0} \int \frac{d\mathbf{k}}{(2\pi)^3} \left[k \frac{c(k)}{\tilde{\Gamma}_0(k)} \right]^2 \phi_s(-k, t) \phi(k, t) S(k). \quad (31)$$

The above relation then serves as the key link between the DFT description of the harmonic solid and the mode coupling kernel. In the ergodic state $\tilde{\gamma}_\infty \rightarrow 0$ and hence α vanishes corresponding to the liquid state. The equation (30) for α is now obtained in the form

$$\alpha_{\text{MCT}} = \frac{1}{6\rho_0} \int \frac{d\mathbf{k}}{(2\pi)^3} \left[k \frac{c(k)}{\tilde{\Gamma}_0(k)} \right]^2 f_s(k) f(k) S(k) \quad (32)$$

Having discussed the two models we are now able to test the equivalence of the two models by comparing the numerical results for α_{DFT} and α_{MCT} obtained for a simple hard sphere system using the DFT and the MCT respectively.

V. NUMERICAL RESULTS

We use the density functional model to compute the α_{DFT} which sets the extent of mass localization in the metastable state. The inhomogeneous density defined in Eqn. (5) is chosen to evaluate the free energy functional (4). The density distribution in a highly inhomogeneous state of the liquid is represented by sharply peaked Gaussian functions centered around each of the lattice sites. The locations of the centers for the Gaussian density profiles, $\{\mathbf{R}_i\}$ distributed on a random lattice, is an input required for the density function. Assuming that the Bernal's random structure [35] is a good approximation for describing the supercooled liquid structure, we use the site-site correlation function $g(R)$ of the corresponding random structure. This pair correlation is determined using the Bennett's algorithm [36] and has been used in earlier DFT studies [7, 9] for describing typical glassy structures. Following Baus and Colot [37], we use the random structure $g_s(R)$ through the following relation

$$g_s(R) = g_B[R(\eta/\eta_0)^{1/3}], \quad (33)$$

where η denotes the average packing fraction and η_0 is used as a scaling parameter for the structure such that at $\eta = \eta_0$ Bernal's structure $g_B(R)$ is reproduced. $g_B(\mathbf{R})$ is computed by averaging over the site-site correlations obtained by taking different points as origin throughout the random structure. The mapping of the function from $\bar{R} = R(\eta/\eta_0)^{1/3}$ to R allows the structure to either dilute or contract depending on the scaling parameter η_0 . The set of lattice sites $\{\mathbf{R}_i\}$ found in computer simulation studies for average positions of particles has also been used in searching the free energy minimum [38]. Similar metastable minima of the free energy functional as above has been observed from such studies as well. In this asymptotic limit corresponding to large α , the ideal gas part of free energy (Eqn.(2)) reduces to,

$$\beta \Delta f_{id}[\rho] \approx - \left[\frac{3}{2} + \ln \rho_0 - \frac{3}{2} \ln \left(\frac{\pi}{\alpha} \right) \right]. \quad (34)$$

The above formula is obtained by replacing the summation inside the logarithmic term by just the contribution from the nearest site. This reduction is not valid for the weakly localized state of the amorphous structure where the α values are small. In this case the gaussian functions centered at different lattice sites are wide enough to cause considerable overlap and the above reduction can no longer be justified. Thus in the range of small α we numerically evaluate the equation (2) and the asymptotic form given in Eqn. (34) is used in

the large α regions. In our earlier work [10] we have shown that these two expressions start merging for typically $\alpha > 40$ within 1%. Similarly we also evaluate the excess contribution to the free energy by expanding around the uniform liquid state. The excess contribution to the free energy therefore depends on the structure of the uniform liquid which is described in terms of the direct correlation function $c(r)$. For the $c(r)$, we have used the Percus-Yevick (PY) form with Verlet-Weiss correction as obtained by Henderson and Grundke [39, 40]. We display in Fig. 2 the direct correlation function $c(r)$ at $\eta = .524$ with and without the Verlet-Weiss correction. These results for the uniform liquid structure is used for both DFT as well as the MCT based calculations which are to be presented in the following. We also display the corresponding results for $g(r)$ for r/σ between 2 and 4, in the inset of Fig. 3.

The free energy functional $F[\rho]$ is computed for different choices of the test density function $\rho(\mathbf{r})$ which is dependent on the localization parameter α . We consider how the free energy surface changes at a fixed packing η for different input structures characterized by the inhomogeneous density $\rho(\mathbf{r})$. For a fixed packing fraction, we calculate the $F[\rho]$ as a function of the parameter η_0 . There are two minimum of the free energy at two respective values of the width parameter α . The first minimum corresponding to a relatively smaller value of α represents a metastable state with low degree of mass localization compared to the second minimum which appears at a larger $\alpha\sigma^2$ value. Different choices of η_0 in the pair correlation function $g_s(R)$, defined in Eqn. (33), are equivalent to choosing different underlying structures for the amorphous lattice depicting the centers of the gaussian density profiles. Testing the free energy dependence on α at a fixed η , we find that the two minima form persists only over a range of η_0 . The free energy curves for different η_0 corresponding to a fixed packing fraction $\eta = .597$ is shown in Fig. 4. The optimum α at the minimum of the free energy is termed as α_{DFT} . The low and high α_{DFT} minima are referred to here as α_{L} and α_{H} . The mean square displacement is defined as $\ell = 1/\sqrt{\alpha_{\text{DFT}}}$. The dependence of the mean square displacement ℓ on η_0 (at a fixed value of η) is displayed in Fig. 5.

Having seen the basic relation between the free energy surface and the localization parameter α we set to compare the MCT and DFT approaches to single particle dynamics in the supercooled state. With increased packing the free energy minimum with high α signifying the sharply localized particle configurations get more stable. We compare between a) the mass localization parameter α_{DFT} calculated using the DFT and b) the corresponding value of α obtained from Eqn. (32) using dynamical approach of MCT. In Fig. 6 the results for

the localization parameters obtained using the DFT and MCT respectively are shown. As the packing fraction increases the density profiles are sharper, *i.e.*, the optimum α increases. For the variation of η along the curve shown in Fig. 6 we change the parameter η_0 with η so as to keep the ratio $\gamma_0 = (\eta/\eta_0)^{1/3}$ remains fixed at .97. The free energy curves for the corresponding pairs of η and η_0 values are shown in Fig. 7. For each of these respective free energy curves in Fig. 7, the corresponding MCT value of α at the same packing fraction, is indicated on the α -axis with a vertical arrow. The position of the arrow depicts the corresponding α_{MCT} which is calculated using model of completely localized single particle dynamics. It appears to be close to the corresponding α_{DFT} for the metastable minimum having the *sharply* localized density profiles. Fig. 8 shows how the localization lengths ℓ for the particles corresponding to the high and low α_{DFT} metastable states depends on packing fraction η . The less localized minimum (corresponding to small α values) is more robust below packing fraction .60. With increasing packing fraction, the sharply localized state (corresponding to large α values) becomes more stable. In Fig. 9 we show (with an arrow at $\eta \approx .60$) the cross over in the relative stability by plotting the difference of the two free energies with respect to packing fraction η . In Fig. 10 we display how the height \mathcal{B}_f of the barrier to cross over from the metastable to state at finite α to the uniform liquid state (at $\alpha \rightarrow 0$) grows with increase of packing fraction.

VI. DISCUSSION

For the single particle in the supercooled state, the average potential energy of the oscillator is given by $\kappa x^2/2$. Application of the equipartition law obtains a relation between the spring constant κ and the width parameter α . This estimation is therefore based on the basis of a static harmonic potential for the single particle dynamics. The same spring constant and hence the natural frequency of the oscillator is also obtained using the MCT approach. The simplest form of MCT predicts an ergodic-nonergodic transition in the supercooled liquid. Beyond the transition, in the non-ergodic state, the single particle correlation decays like a harmonic wave. The frequency of the wave is related to the long time limit of the memory function [21] corresponding to the correlation of single particle densities. This links natural frequency of oscillation and hence the memory function is related to the spring constant κ . The width parameter α of DFT is thus related to the long time limit of the

memory function.

Phenomenological relation between structural properties and transport coefficients of a liquid has earlier been observed [44, 45]. In the present work, we find agreement between the static and dynamic models of the metastable liquid in which the particle positions are localized over time scales of structural relaxation. This is concluded from the close agreement obtained for the width parameter α in the respective theoretical models of the DFT and MCT. The primary connection between the DFT and MCT formulations is the free energy functional $F[\rho]$ which appears in the formulation of either model. The free energy determines both the structure as well as the dynamics. In the thermodynamic approach the local minima of $F[\rho]$ represent the metastable states. In the dynamic approach the same free energy functional is key to the form of the nonlinear couplings in the equations of generalized hydrodynamics. These nonlinearities are the essential ingredient in construction of the memory functions for the dynamics. The self consistent expression for the memory functions constitute the MCT with the feedback mechanism that causes the ENE transition at a critical density. In the nonergodic state the single particle motion is localized. Hence in our comparison, using the same free energy functional in constructing both the DFT and the MCT models is essential. However the approximate free energy functional (4) is not good when the density fluctuations are large, which is more the case near freezing point T_m . With the strongly localized density profiles of the amorphous state, this same concern remains. In this regard the DFT has been improved using weighted density functional [41, 42] models. In such models the localization parameter changes significantly. However to compare with the MCT results would then also require changing the mode coupling vertex functions in the dynamic model accordingly. Furthermore, in the present work the density profiles are assumed to be described by gaussian profiles and all non-gaussian behavior are ignored [43].

From the density functional approach it emerges that the free energy functional expressed in terms of density fluctuations, have two qualitatively different types of minimum [10]. The minimum of the $F[\rho]$ corresponding to a lower degree of mass localization (at lower α value) is generally more stable than the state with sharply localized density profiles (higher α values). Both minima (low and high α values) represents particle localization and hence conforms to a nonergodic state. However as we note from the results of Fig. 6-7, this less localized minimum corresponds to a higher mean square displacement for the tagged particle than what is predicted for the nonergodic state obtained from a simple one loop MCT for self

correlations [22]. This can possibly be an outcome of the simple adiabatic approximation we have adopted [22] in evaluating the corresponding memory function for the single particle dynamics. Over intermediate time scales however, the interpretation of sharp localization given in Ref. [23] for the high α minimum and hence agreement the simple MCT models holds. This similarity between the two microscopic models for describing the physics of supercooled liquid is a signature of the consistency in the respective approach. Over asymptotically long time scales the particle should get out of the non ergodic state [46, 47]. We have not considered here the mechanisms which might lead to spontaneous breaking of ergodicity in the supercooled liquid. With this an exponentially large number of metastable states appear for intermediate free energy values and gives rise to finite configurational entropy [48] for the system.

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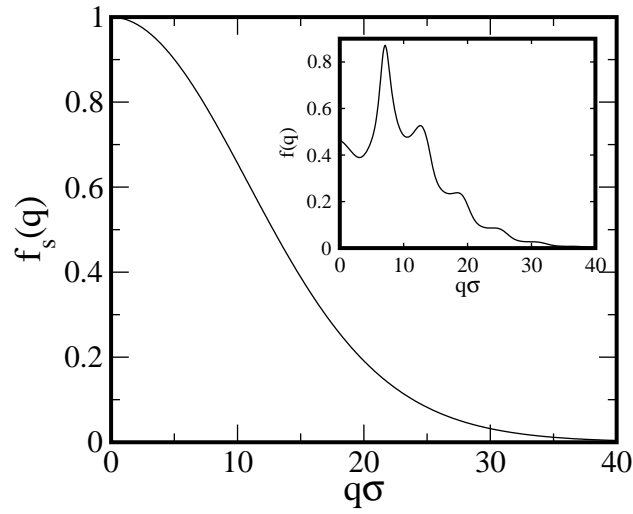


FIG. 1: Non ergodicity parameters f_s for self and f for total correlation functions shown as the main and inset at $\eta = .525$.

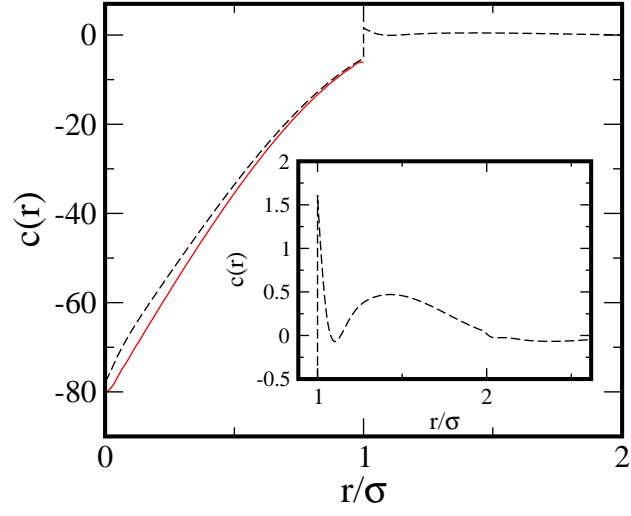


FIG. 2: The pair correlation function $c(r)$ with Verlet-Weiss correction (solid) and without (dashed) for the uniform liquid at packing $\eta = .524$. Inset is an enlarged view

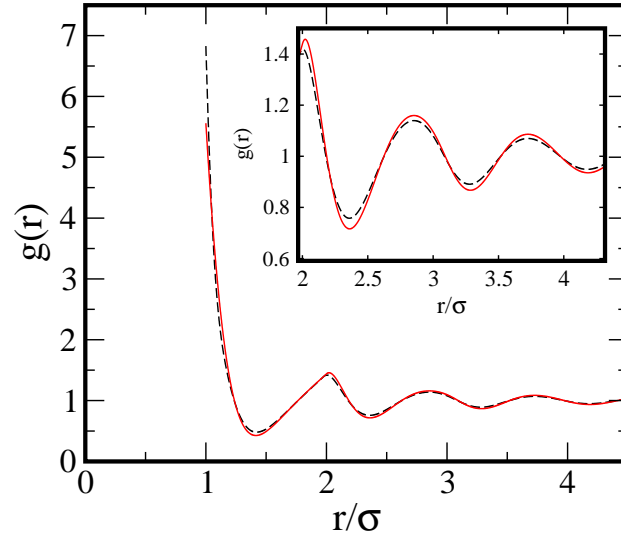


FIG. 3: The pair correlation function $c(r)$ with Verlet-Weiss correction (solid) and without (dashed) for the uniform liquid at packing $\eta = .524$. Inset is an enlarged view

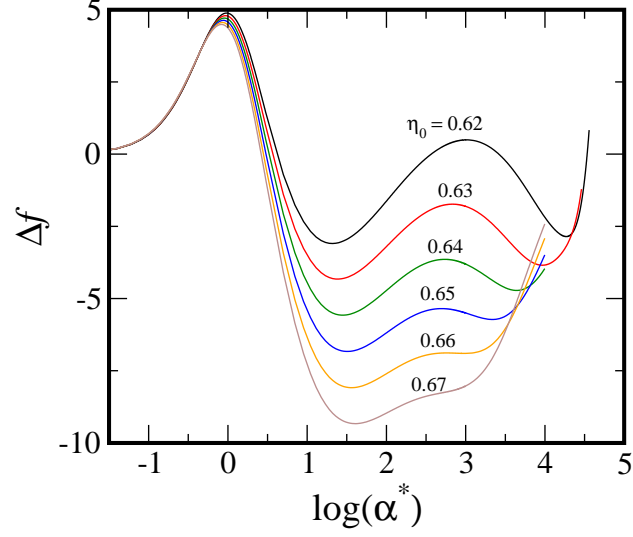


FIG. 4: Free energy vs. α at fixed $\eta = .597$ for different structures characterized in terms of the parameter η_0 (see text) as indicated with the corresponding curve.

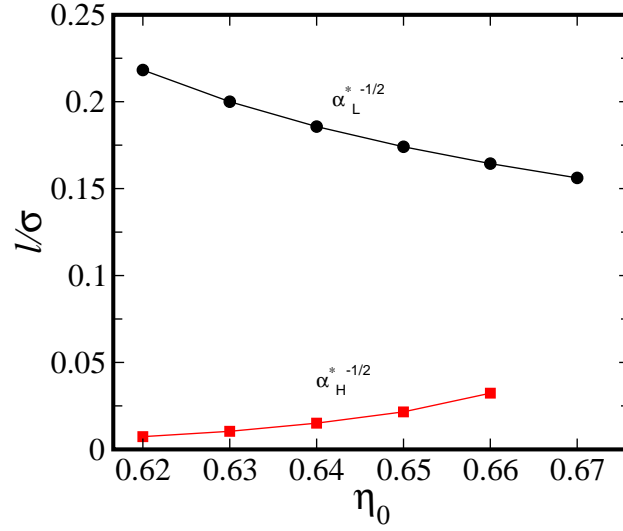


FIG. 5: The average mean square displacement ℓ in units of hard sphere diameter σ , for both high localization and low localization vs η_0 (see text), corresponding to the packing fraction $\eta = .597$.

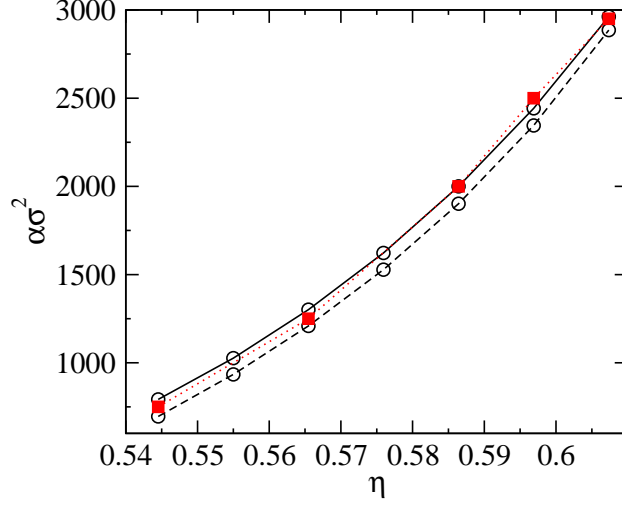


FIG. 6: Comparison of the width parameter values (in units of σ^{-2}) from DFT (filled squares) and MCT (open circles). α_{MCT} obtained from MCT using as input Percus Yevick structure factors with (dashed) and with out (solid) the Verlet-Weiss correction. The result α_{DFT} obtained from DFT is shown as dotted line.

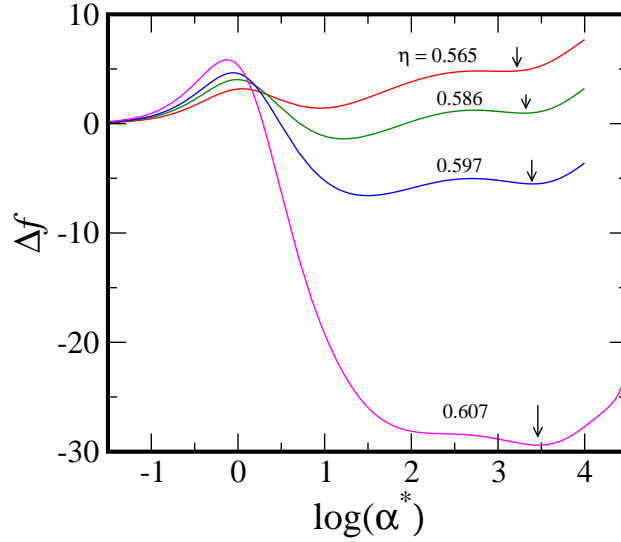


FIG. 7: Free energy vs. α for different packing fractions η denoted in Fig. 6. The position of the corresponding minima at large α is shown with a vertical arrow for each free energy curve

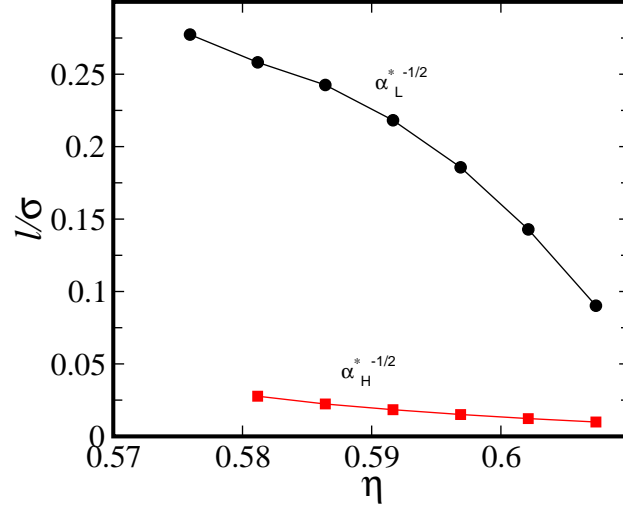


FIG. 8: The average mean square displacement ℓ in units of hard sphere diameter σ , for both high localization and low localization vs packing fraction η , corresponding to the results shown in Fig. 6.

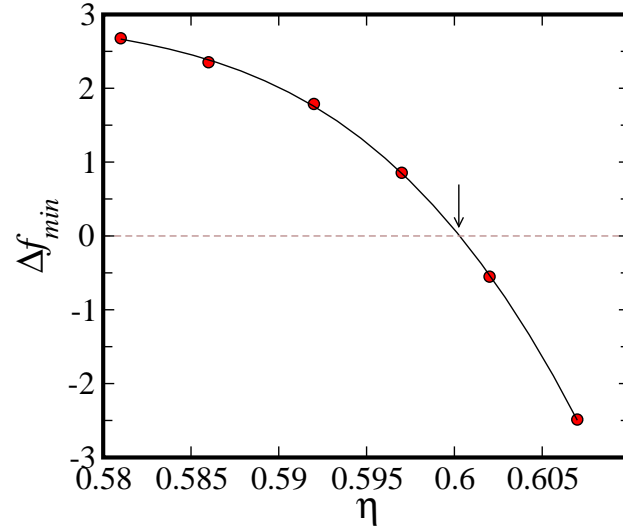


FIG. 9: The difference of the free energy minima at low and high values of α as shown in Fig. 6 vs packing fraction η corresponding to the results shown in 6.

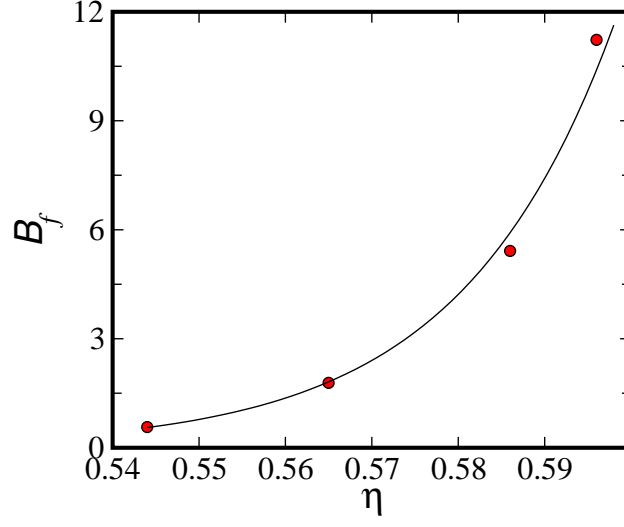


FIG. 10: The barrier in free energy \mathcal{B}_f measured from the low α minimum, to cross to the uniform liquid state at $\alpha = 0$ vs. packing fraction α . The line shows a power law fitting $(\eta_c - \eta)^{-a}$